

Cassia grandis seed gum-graft-poly(acrylamide)-silica hybrid: An excellent cadmium (II) adsorbent

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Received: 28 July 2014, Revised: 11 September 2014 and Accepted: 24 October 2014

ABSTRACT

This study puts forward the synthesis of an excellent cadmium adsorbent having unprecedented high capacity ($Q_{\max} = 5000 \text{ mg g}^{-1}$) to capture cadmium ions from synthetic cadmium solution. To synthesize the adsorbent (A_{700}), base catalyzed polymerization of tetra ethylorthosilicate (TEOS) was conducted under the sacrificial templation effect of poly(acrylamide) grafted *Cassia grandis* seed gum (CG) while using H_2O , TEOS and EtOH in 8:1:1 ratio (v/v). The CG inspired adsorbent was characterized by FTIR, XRD and SEM, both before and after cadmium adsorption. The adsorption parameters for the synthesized adsorbent were optimized by performing the batch adsorption studies under different pH, initial cadmium concentration, adsorbent dose, and contact time. The adsorption showed pseudo second order kinetics with a rate constant of $1.55 \times 10^{-4} \text{ g mg}^{-1} \text{ min}^{-1}$ at 450 mg mL^{-1} Cd(II) concentration. The thermodynamic study showed that the adsorption is endothermic and spontaneous. The adsorbent could be successfully reused for three cycles. The present adsorbent is not only very efficient in cadmium uptake; it is greener than the contemporary porous silica adsorbents derived through templation of pure synthetic polymers or surfactants. Moreover the source polysaccharide used for its synthesis is abundant and cheap. This hybrid can utilized as versatile and sustainable adsorbent for cadmium recovery from industrial wastes. Copyright © 2015 VBRI Press.

Keywords: Tetraethylorthosilicate; *Cassia grandis*-graft-polyacrylamide; Cd(II) adsorbent.



Vandana Singh is Associate Professor of Chemistry at Department of Chemistry, University of Allahabad, India. She has >20 years of teaching experience and her research interest is polysaccharide based macromaterials. She could evolve greener methods for polysaccharide transformations such as methylation, hydrolysis and grafting. She has been ranked first among the top ten world scientists working on Guar gum. She is editor of *Green Chemistry for Environmental*

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Introduction

The development and applications of new organic/inorganic hybrid materials prepared by the sol-gel approach is rapidly becoming a fascinating new field of research in materials science [1]. The biomineralization processes regulated by proteins and polysaccharides

leading to silica synthesis are widely spread in nature [2]. Hybrids with organic and inorganic interface are of special interest to researchers as they are multifunctional materials with tailored properties. Such bioinspired materials with organic-inorganic interface possess properties such as good permeability, selectivity, mechanical strength, and thermal and chemical stability.

Seed gums are galactomannan polysaccharides having a backbone of β -D(1 \rightarrow 4) mannopyranosyl units attached to α -D-galactopyranosyl units as the side chains [3-5]. The galactomannans [6] in their native and derived form find use in various industries and many of them are popular as industrial gums e.g. guar gum [6,7]. The repeating units of these seed gums differ from each other in having different galactose to mannose ratios and molecular weights. Their chemical properties may be utilized towards the development of various versatile materials for commercial use. The properties of these gums have been enhanced by chemical modifications, grafting of polymeric units and by incorporating inorganic components, depending upon the application in question. Since the ratio difference of the component monosaccharides can drastically affect the properties of the seed gums, the scope of utilization of these gums is endless. Many of the vinyl modified polysaccharide materials have been used as efficient flocculators [5, 8, 9] and adsorbents for heavy metal ions [10,11]. Recently our group reported lead removal from waste water using methylmethacrylate grafted *Cassia grandis* seed gum [12].

Functionalized porous silicas [13] are known to behave as heavy metal ion adsorbent. Ideally a chemically active adsorbent with high stability and capacity should possess very low solubility in water; sufficient thermal stability, sterically compact geometry and sufficient chemical stability to retain activity during the operation and regeneration. Careful planning and execution of templated silicas can be used as a method of choice in deriving highly selective chemically active adsorbents [14].

The ribbon like conformation of the galactomannans and their copolymers can potentially modify the sol gel process to result into silica hybrids with novel microstructures and morphologies. So far, no attempt has been made towards the preparation of silica adsorbent materials using the copolymeric polysaccharides as templates except by our own group [15, 16] on the novel nanocompositional hybrids derived from vinyl modified guar gum and silica. The materials showed promising results for Zn(II) or/and Cd(II) uptake from aqueous solutions. The vinyl grafts at the polysaccharide played an important role in deciding the adsorbent's performance. The use of poly(acrylamide) grafted guar in place of saponified poly(acrylonitrile) guar gum as template during the sol gel hybrid synthesis from TEOS resulted into exceptionally good Cd(II) adsorbent (Q_{\max} 2000 mg g⁻¹) [17].

The focus of this work was to design an efficient cadmium adsorbent from sol gel polymerization of tetraethylorthosilicate (TEOS) under the sacrificial templation effect of *Cassia grandis* seed gum-graft-poly(acrylamide) (CG-g-PAM). *Cassia grandis* is a nonconventional source of seed gum in which galactose and mannose are present in 1:3 molar ratio [18]. The seed gum differs from guar gum

in its molecular weight and in galactose to mannose ratio, which is 1:2 for the guar gum [15]. The fine structural difference between the two seed gums can be manipulated for tailoring the adsorbent behavior of the silica hybrids derived from them. The hybrid was calcined at various temperatures [14] for a better understanding on the role of the polysaccharide's fine structure in controlling the adsorbent microstructure and performance. The adsorbent behavior of the prepared hybrids was compared and evaluated by taking Cd(II) as representative heavy metal ion where the Cd(II) adsorption capacity of the optimum performance material was investigated using batch adsorption technique.

Present cadmium adsorbent is important as its synthesis utilized a nonconventional galactomannan polysaccharide (*Cassia grandis* seed gum) which is much cheaper and abundant [19] than the pure polymeric or surfactant templates. This is first study of this kind where a copolymer of nontraditional galactomannan polysaccharide has been used as template to develop a porous silica adsorbent for metal ion removal.

Experimental

Materials

Tetraethylorthosilicate (98% TEOS; Aldrich, USA) was used as silica precursor. NH₄OH (30% NH₃; Merck, India) was used. Acrylamide (Merck, India) was recrystallized twice from methanol (GR) and dried in vacuum. Ascorbic acid and potassium persulfate (BDH, India Analar Grade) were used without further purification. AgNO₃ (Merck, India) was used. Cd(NO₃)₂ (Merck, India) was used for preparing stock Cd(II) solution. *Cassia grandis* seed gum was supplied by Himani seed stores, Dehradun, India and identified by systematic botanist at Botanical Survey of India, Allahabad.

Instrumentations

The pH of the solution was measured with a Digital pH meter (pHep Hanna instruments) equipped with a glass working electrode and a reference Ag/AgCl electrode (Systronics model T-105). Infrared (IR) spectra were recorded on a Perkin-Elmer Infrared spectrophotometer making KBr mulls in reflectance mode. XRD was carried out on Rigaku D/MAX-2200 X-ray powder diffractometer. SEM analysis was done on EDAX, FEI Quanta 200 machine. Temperature treatment of the hybrid was performed in Mac (India) electric Muffle Furnace in air. The adsorbed metal ions were determined by titration with 0.01M EDTA using Xylenol Orange as indicator. The amount of metal ions adsorbed per gram of the polymer was calculated by difference between the initial and final concentration of the metal ion in the solutions.

Isolation and purification of the seed gum

Cassia grandis (CG) seeds (1 kg) were exhaustively extracted with light petroleum followed by EtOH to remove fatty and coloring materials and then suspended in 1% aqueous acetic acid overnight. The filtrate of the 1% solution was precipitated with 95% EtOH. The seed gum was reprecipitated thrice from 1% aqueous solution to

obtain a white amorphous product that was purified as described elsewhere [5].

Grafting of the seed gum

To 25 mL of CG gum solution (4g L^{-1}), calculated amount of acrylamide ($11 \times 10^{-2}\text{ M}$), ascorbic acid ($2.3 \times 10^{-2}\text{ M}$) and AgNO_3 ($8 \times 10^{-5}\text{ M}$) (as a catalyst) were added and the reaction mixture was thermostated on thermostatic water bath at $35 \pm 0.2\text{ }^\circ\text{C}$ [20]. After 30 min, $\text{K}_2\text{S}_2\text{O}_8$ ($30 \times 10^{-3}\text{ M}$) was added and this time of addition of persulfate was taken as zero time. Graft copolymerization was allowed for 1 h. Grafted CG gum sample was separated from the reaction mixture by pouring into excess of $\text{MeOH}:\text{H}_2\text{O}$ (7:3). The copolymer sample was finally extracted with $\text{MeOH}:\text{H}_2\text{O}$ in a soxhlet apparatus for 4 h to dissolve all the homopolymer and was finally dried under vacuum at $50\text{ }^\circ\text{C}$ for $>24\text{ h}$ to a constant weight for obtaining *Cassia grandis*-g-poly(acrylamide) (CG-g-PAM) (%G 110; % E 56).

Preparations of CG-g-PAM-silica hybrid

CG-g-PAM (1.0 g) was dissolved in 20 mL of distilled water. Separately a definite amount of TEOS was also dissolved in a known volume of ethanol. A third solution incorporating a known volume of ammonium hydroxide (12 N) was prepared separately. Afterwards, the three solutions were rapidly poured together into a reaction glass flask and kept under gentle stirring for 18 h at room temperature. The mixture was then subjected to slow evaporation at $60\text{ }^\circ\text{C}$ for about 6 h and then 4 h at $80\text{ }^\circ\text{C}$ until a dry material was obtained [16]. A series of hybrids (H_A - H_K) were obtained by changing the $\text{H}_2\text{O}:\text{TEOS}:\text{EtOH}$ ratios, keeping the amount of CG-g-PAM and NH_4OH fixed.

The cadmium binding capacity of the prepared hybrid materials was evaluated in batch adsorption experiments under optimized parameters: adsorbent dose 25 mg, 450 mg mL^{-1} Cd(II) concentration, pH 8, rpm 60 at $35\text{ }^\circ\text{C}$. The hybrid (H_K) synthesized using $\text{H}_2\text{O}:\text{TEOS}:\text{EtOH}$ in 8:1:1 ratio at fixed amount of CG-g-PAM and catalyst showed maximum binding. To understand the effect of the thermal sintering on the adsorption behavior, H_K was the hybrid of choice for further studies. It was further thermally treated inside a muffle furnace in air at $80\text{ }^\circ\text{C}$, $250\text{ }^\circ\text{C}$, $500\text{ }^\circ\text{C}$, $700\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ each for 2 h and the adsorbents so obtained were named A_{80} , A_{250} , A_{500} , A_{700} , A_{800} respectively.

Preparations of control silica

To evaluate the role of polysaccharide, dehydroxylation polymerization of TEOS was allowed in absence of the polysaccharide template. In a manner similar to H_K , the reaction mixture was then subjected to slow evaporation at $60\text{ }^\circ\text{C}$ for about 5-6 h and then 3-4 h at $80\text{ }^\circ\text{C}$ until a dry material was obtained. This was further heat treated inside furnace at $250\text{ }^\circ\text{C}$, $500\text{ }^\circ\text{C}$, $700\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ for 2 h at each temperature to obtain control adsorbents devoid of polysaccharide (C_{80} , C_{250} , C_{500} , C_{700} , C_{800} , respectively).

Adsorption batch experiments

The Cd(II) binding capacities of both, heat treated hybrids (A_{80} , A_{250} , A_{500} , A_{700} , A_{800}) and control silicas (C_{80} , C_{250} , C_{500} ,

C_{700} , C_{800}) were evaluated by batch adsorption studies from synthetic aqueous solutions.

Stock solutions of standard Cd(II) (1000 mg mL^{-1}) were prepared from $\text{Cd}(\text{NO}_3)_2$ in distilled-deionised water. Adsorption experiments were carried out using the synthesized materials in a temperature controlled incubator shaker set at 60 rpm maintained at $35\text{ }^\circ\text{C}$ for 2.5 h. A known amount of adsorbent was thoroughly mixed with 50 mL of respective Cd(II) solutions, whose concentrations and pH values were previously known. pH of the reaction mixture was initially adjusted using either hydrochloric acid (1 M) or sodium hydroxide (1 M). After the flasks were shaken for the desired time, the suspensions were filtered through Whatman 0.45 mm filter paper and the filtrates were analyzed for the Cd(II) concentration by titration with 0.01M EDTA using Xylenol Orange as indicator [21].

The amount of metal ions adsorbed [17] per gram of the adsorbent was calculated by the difference between the initial and the final readings using the following equation.

$$q_e (\text{mg g}^{-1}) = C_0 \cdot C_e (\text{mg L}^{-1}) \times V (\text{L}) / W(\text{g}) \text{ ----- (1)}$$

Where q_e is the amount of the cadmium adsorbed (mg g^{-1}) on the adsorbent, C_0 , the initial concentration of Cd(II) (mg L^{-1}), C_e , the equilibrium concentration of Cd(II) in solution (mg L^{-1}), V , the volume of the solution used (L), and W , the weight of the adsorbent used.

The adsorption was optimized using the optimum performance sample (A_{700}). The pH, initial concentration of Cd (II), adsorbent dose, contact time and the electrolyte amount (ionic strength) were varied, one at a time while keeping the other parameters fixed.

For pH studies, 50 mL of 450 mg mL^{-1} Cd(II) solutions were adjusted to various pH ranging from 1 to 12 and the optimum pH was determined using 25 mg adsorbent dose. To study the effect of initial Cd(II) concentration, the range for different initial cadmium concentrations used were 225 mg mL^{-1} to 2023 mg mL^{-1} at 25 mg adsorbent dose. Effect of adsorbent dose on the adsorption was studied in the range of 25-125 mg. In order to evaluate kinetic data, the agitation time was varied from 30 minutes to 150 min and the kinetic studies were performed at 450 mg mL^{-1} initial Cd(II) concentration using 25 mg adsorbent dose. Separate flasks were prepared for each time interval and only one flask was taken for desired time. Unless otherwise stated the experiments were carried out at 450 mg mL^{-1} Cd(II) concentration, 25 mg adsorbent dose, 50 mL working volume, 60 rpm and 2.5 h shaking time.

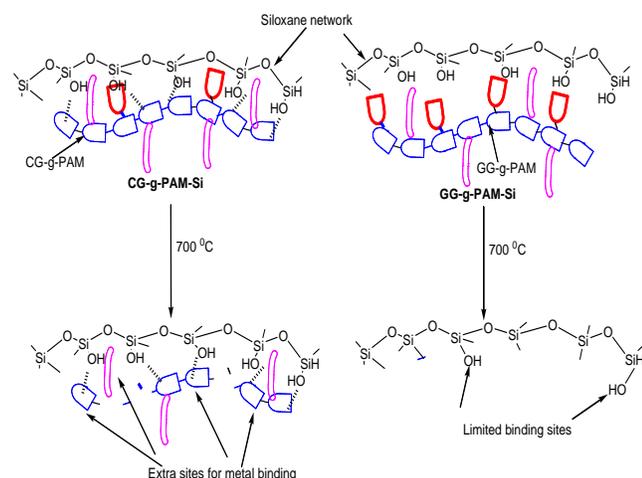
Desorption studies

In order to determine the reusability of the A_{700} , Cd(II) was stripped off from the spent A_{700} using 2 M H_2SO_4 and reused. For the stripping, the Cd(II) loaded A_{700} was placed in the 2 M H_2SO_4 and stirred at 130 rpm for 2 h at $30\text{ }^\circ\text{C}$ and the final Cd(II) concentration was determined. After each cycle the used adsorbent was washed well with distilled water and used in the succeeding cycle. The amount desorbed was calculated from the amount of metal ions loaded on the adsorbent and the final cadmium concentration in the stripping medium. After successive

leaching, the adsorbent was used two more times using 25 mg of the composite and 450 mg mL⁻¹ initial Cd(II) solution in total volume of 50 mL, 60 rpm, 35 °C.

Results and discussion

The hybrid (H_K) (Table 1) synthesized using H₂O:TEOS:EtOH in 8:1:1 ratio at fixed amount of CG-g-PAM and catalyst showed maximum cadmium binding (Scheme 1). H_K hybrid along with the control silica was dried and calcined in air at 80 °C, 250 °C, 500 °C, 700 °C and 800 °C for 2 h at each temperature. The calcined materials were evaluated for batch adsorption and reusability studies (Table 2).



Scheme 1. A plausible explanation for Cd(II) binding by CG-g-PAM-Si in comparison to GG-g-PAM-Si.

Table 1. Cd(II) adsorption by different hybrids synthesized at pH 8, 450 mgL⁻¹ Cd(II) initial concentration, adsorbent dose 25 mg, rpm 60, temperature 35 °C, adsorbent dose 50 mg.

Hybrid	CG-g-PAM (g)	H ₂ O (mL)	TEOS (mL)	EtOH (mL)	Ratio H ₂ O:TEOS:EtOH	Ads in [Cd(II)] mgL ⁻¹
H _A	1.0	10	1.5	1.5	6.6:1:1	370.92
H _B	1.0	15	1.5	1.5	10:1:1	377.66
H _C	1.0	20	1.5	1.5	13.3:1:1	386.66
H _D	1.0	25	1.5	1.5	16.6:1:1	388.90
H _E	1.0	20	1.0	1.5	20:0.66:1	382.16
H _F	1.0	20	2.5	1.5	8:1.6:1	413.63
H _G	1.0	20	3.0	1.5	6.6:2:1	409.14
H _H	1.0	20	2.5	1.0	8:2.5:1	409.14
H _I	1.0	20	2.5	1.5	8:1.6:1	413.63
H _J	1.0	20	2.5	2.0	8:1.25:1	427.12
H _K	1.0	20	2.5	2.5	8:1:1	445.14

It is evident from Table 2, that calcinations up to 700 °C to enhanced the adsorption potential of the hybrids, while further increase in calcination temperature decreased the adsorption which can be attributed to the decrease in porosity of the hybrid as a result of transpore condensation within the siloxane domains

The cadmium adsorption by A₇₀₀ was optimized by varying the process parameters of the batch adsorption

experiments. The maximum Cd²⁺ adsorption that could be reached was 98.8 % using 25 mg adsorbent dose, 450 mg mL⁻¹ initial cadmium concentration, 60 rpm, 2.5 h contact time, 50 mL contact volume at 35 °C. The poly(acrylamide) grafted CG gum offered appropriate templating environment for the ensuing porous siloxane network.

Table 2. Adsorption of Cd(II) using the composite and silica calcined at different temperatures at 450 mg L⁻¹ initial Cd(II) concentration, pH = 8, adsorbent dose 25 mg, rpm 60, contact time 2.5 h, total volume 50 mL at 35 °C.

Calcination temperature (°C)	Adsorption by the Hybrids (A ₈₀ , A ₂₅₀ , A ₅₀₀ , A ₇₀₀ , A ₈₀₀) (mg L ⁻¹)			Adsorption by Control Silica (C ₈₀ , C ₂₅₀ , C ₅₀₀ , C ₇₀₀ , C ₈₀₀) (mg L ⁻¹)		
	1 st cycle	2 nd cycle	3 rd cycle	1 st cycle	2 nd cycle	3 rd cycle
80	292.24	291.12	289.43	213.56	210.89	205.69
250	325.96	323.71	322.59	207.94	204.57	202.32
500	359.68	357.86	355.75	139.38	135.44	133.19
700	445.14	442.86	441.17	128.14	124.2	122.52
800	438.36	436.11	434.99	119.15	115.77	114.09

To the best of our knowledge, the adsorption capacity of A₇₀₀ was found to be far superior to any of the previously reported cadmium adsorbents. More over the adsorbent attained equilibrium in just 2.5 h and its performance was 2.5 times higher than the similarly derived guar-graft-poly(acrylamide)-silica nanocomposite synthesized [17] by our group (Table 3). The huge difference in adsorption capacities of similarly derived nanohybrids may be attributed to different structure of the repeating units of the two polysaccharides (Fig. 1). The repeating unit structure (Fig. 1) of the two polysaccharides indicates that *Cassia grandis* seed gum has galactose side chains after every two mannose units at the mannose main chain, while the guar gum has galactose branching at every alternate mannose units. More frequent branching in the guar gum is likely to diminish the association between the mannan hydroxyls at the backbone with the surface silanols of silica matrix (Scheme 1) due to steric reasons. It appears that due to stronger association, CG-g-PAM escaped in small pieces, leaving back few tightly associated fragments attached to the hybrid pore wall to offer extra sites for the metal ion binding but this assumption needs further study and experimental evidences. The weaker association of GG-g-PAM with silanols at the ensuing silica matrix might have allowed an easy escape of GG-g-PAM from the siloxane network structure on calcination.

Table 3. Comparison of silica hybrids synthesized from Guar-g-PAM and CG-gum-g-PAM (A₇₀₀).

Composite	Gal: Man Ratio in the seed gum	H ₂ O:TEOS:EtOH	b	Q _{max} (mg g ⁻¹)	R _L at 100 mg mL ⁻¹	Ref
GG-g-PAM-Si	1:2	16:2:1	0.0495	2000	0.6688	17
CG-g-PAM Si	1:3	8:1:1	.03225	5000	0.2367	Current study

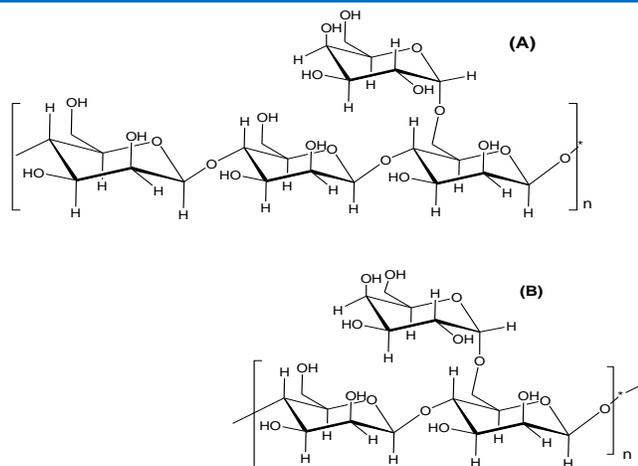


Fig. 1. Structure of the repeating unit of *Cassia grandis* (A) in comparison to repeating unit structure of guar gum (*Cyamopsis tetragonolobus*).

Optimization of adsorption conditions

Cd(II) adsorption conditions for A₇₀₀ has been optimized by changing the various parameters of the batch experiment, one at a time while keeping the others fixed (**Fig. 2**).

Effect of pH on Cd (II) adsorption

The effect of pH on Cd (II) adsorption was studied in the range of pH 1-12 using 25 mg adsorbent dose, 450 mg mL⁻¹ initial Cd(II) concentration, 60 rpm, 2.5 h contact time, 50 mL contact volume at 35 °C. It was observed that the extent of Cd(II) removal by A₇₀₀ increased (from 112 to 445 mg mL⁻¹) with the increase of pH and was maximum at pH 8 (445 mg mL⁻¹), which again decreased as the pH was further increased (from 445 to 415 mg mL⁻¹). This decrease can be explained by the precipitation of Cd(OH)₂ at pH>8. Effect of pH on Cd²⁺ adsorption is summarized in **Fig. 2(A)**.

Effect of concentration of Cd²⁺.

The effect of initial Cd(II) concentration was studied at pH 8, 60 rpm, 2.5 h contact time, 25 mg adsorbent dose at 35 °C. It was observed that with the increase in the initial concentration of Cd²⁺ from 250 mg mL⁻¹ to 2023 mg mL⁻¹, the adsorption increased (from 225 mg mL⁻¹ to 1821 mg mL⁻¹). At higher initial Cd²⁺ concentration, more Cd(II) is available for the binding on the binding sites at the adsorbent, which are fixed. The effect of initial Cd (II) concentration on the adsorption has been shown in the **Fig. 2(B)**.

Effect of adsorbent dose on Cd²⁺ adsorption

The effect of adsorbent dose on Cd²⁺ removal was studied in the range of 15-100 mg per 50 mL at 450 mg mL⁻¹ initial cadmium concentration. The percentage Cd(II) removal by A₇₀₀ increased on increasing the dose from 15-25 mg (from 402 mg mL⁻¹ to 445 mg mL⁻¹) and further increase in the adsorbent dose did not affect the adsorption much therefore 25 mg dose was chosen for the optimization of the adsorption (**Fig. 2C**).

Effect of rpm on Cd²⁺ adsorption

Variation in rpm was studied in the range of 60-200 at 450 mg mL⁻¹ initial Cd(II) concentration, pH 8, 2.5 h contact time, 25 mg adsorbent dose at 35 °C, where optimum adsorption was seen at 60 rpm (445 mg mL⁻¹) and therefore all the studies were performed at 60 rpm. Increasing the rpm beyond 130, decreased the adsorption. The adsorption decreased from 421 to 395 mg mL⁻¹ on increasing the rpm from 130 to 200, which indicated some desorption taking place at high rpm (**Fig. 2D**).

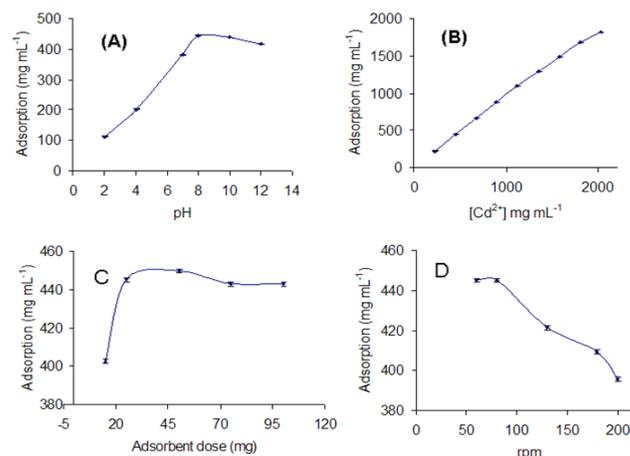


Fig. 2. Optimization studies with A₇₀₀ as adsorbent. (A) Effect of pH at 25 mg adsorbent dose, 450 mg mL⁻¹ Cd(II), 60 rpm, 2.5 h contact time, in 50 mL solution at 35°C; (B) Effect of initial Cd(II) concentration at pH 8, 60 rpm, 2.5 h contact time, 25 mg adsorbent dose at 35 °C; (C) Effect of adsorbent dose at 450 mg mL⁻¹ initial Cd(II), pH 8, 60 rpm, 2.5 h contact time, at 35 °C; (D) Effect of rpm at 450 mg mL⁻¹ initial Cd(II) concentration, pH 8, 2.5 h contact time, 25 mg adsorbent dose at 35 °C.

Effect of electrolytes

The effect of electrolyte (NaCl and Na₂SO₄) on the Cd (II) removal by A₇₀₀ was studied (Figure not shown). With increase in concentration of both NaCl and Na₂SO₄ (from 0.01M to 1.0 M), the removal decreased from 427 to 391 mg mL⁻¹ and from 422 to 382 mg mL⁻¹ respectively from 50 mL of 450 mg mL⁻¹ Cd(II) solution at pH 8, temperature 30 °C, rpm 60 and contact time 2.5 h. The decrease in the removal on increasing the electrolyte concentration may be due to the competition between cadmium species and SO₄²⁻/Cl⁻ at the binding sites of silica matrix, where SO₄²⁻/Cl⁻ ion can be electrostatically held on silicon atom.

Adsorption isotherm studies

Adsorption data were fitted to the Langmuir and Freundlich isotherms [17].

The Langmuir isotherm is valid for monolayer sorption due to a surface of a finite number of identical sites and expressed in the linear form as under.

$$C_e/q_e = 1/bQ_0 + C_e/Q_0 \quad (2)$$

Where C_e is the equilibrium concentration (mg L⁻¹) and q_e the amount adsorbed at equilibrium (mg g⁻¹). The Langmuir constants Q_0 (mg g⁻¹) represent the monolayer adsorption capacity, and b (L mg⁻¹) relates the heat of adsorption.

The essential feature of the Langmuir adsorption can be expressed by means of R_L , a dimensionless constant referred to as separation factor or equilibrium parameter for predicting whether an adsorption system is favorable or unfavorable. R_L is calculated using the following equation

$$R_L = 1/1 + bC_0 \quad (3)$$

Where C_0 is the initial Cd(II) concentration (mg L^{-1}). If R_L values lies between 0 and 1, the adsorption is favorable.

The Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as:

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (4)$$

Where K_f indicates adsorption capacity (mg g^{-1}) and n an empirical parameter related to the intensity of adsorption, which varies with the heterogeneity of the adsorbent. The greater the values of the $1/n$, better is the favorability of the adsorption.

The equilibrium data fitted to langmuir model and freundlich models at 35 and 15 °C where the data fitted better in Langmuir isotherm indicating surface homogeneity of the adsorbent and unilayer adsorption (Fig. 3).

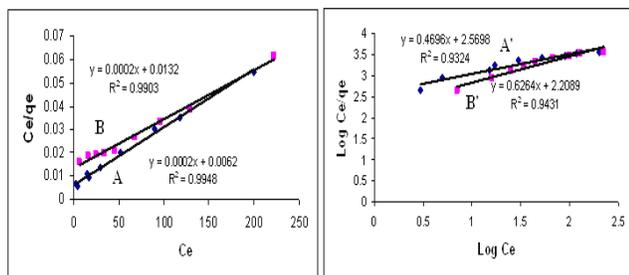


Fig. 3. Langmuir isotherm (A) at 35 °C and (B) at 15 °C and Freundlich isotherm (A') at 35 °C at 15 °C.

At both the temperatures, Q_0 was calculated (from Langmuir isotherm) to be 5000 mg g^{-1} indicating that the adsorbent had a very high capacity to remove Cd (II) ions (Fig. 3). The R_L value was 0.0645 (at 450 mg L^{-1} Cd(II)) indicating the adsorption to be favorable. The Langmuir constant b (and Freundlich constant (K_f)) increased with increasing temperature from 15 to 35 °C implying that the adsorption process was endothermic in nature. The value of Langmuir constant b increased with temperature thereby suggesting that the Cd(II) exhibited higher affinity for the adsorbent at higher temperature than at lower temperature. The value of n is found to be >1 , that indicated that the adsorption of Cd(II) onto the composite was favorable. The Q_{\max} for the composite was found 2.5 time higher than the material derived from guar-g-poly(acrylamide) where the optimum sorbent was obtained by using $\text{H}_2\text{O}:\text{TEOS}:\text{EtOH}$ in 16:2:1 ratio and sintering the composite to 600 °C the two hybrids have been compared in Table 4. It is also higher than other reported adsorbents (Table 5).

Sorption kinetics

Cd(II) adsorption was monitored with time. The kinetic study revealed that the adsorption was initially rapid which

attained a state of equilibrium within 2.5 h and thereafter no adsorption took place up to 4 h. The initial rapid adsorption can be attributed to the large number of available vacant sites which generated an increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent [22]. Gradually the adsorption sites decreased which in turn resulted into decreased adsorption. Initial rapid adsorption indicated a surface reaction process is taking place. Kinetics [23] of the adsorption was modeled by the first order Lagergren equation, the pseudo-second-order equation and the second-order rate equation shown below as Eqs. (5)–(7), respectively (Fig 4).

$$\frac{\text{Log}(q_e - q_t)}{q_e} = \text{Log } q_e - \frac{k_L t}{2.303} \quad \text{-----} \quad (5)$$

$$t/q_t = 1/k' q_e^2 + t/q_e \quad \text{-----} \quad (6)$$

$$1/(q_e - q_t) = 1/q_e + k_2 t \quad \text{-----} \quad (7)$$

Where K_L is the Lagergren rate constant of adsorption (min^{-1}); k' the pseudo-second-order rate constant of adsorption ($\text{g. mg}^{-1}. \text{min}^{-1}$) and k_2 the second-order rate constant ($\text{g. mg}^{-1}. \text{min}^{-1}$); q_e and q_t are the amounts of metal ion sorbed (mg g^{-1}) at equilibrium and at time t , respectively. Kinetic data of Cd(II) adsorption by A_{700} fitted best in to pseudo second order kinetic equation, where linear plot of t/q_t vs t was obtained with the correlation coefficient (R^2) being 0.9999 and rate constant 1.282×10^{-4} at 450 mg mL^{-1} Cd(II) concentration (Fig. 4).

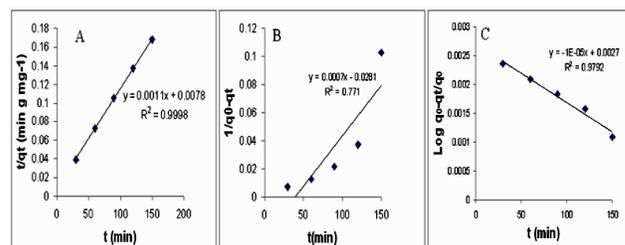


Fig. 4. (A) pseudo second order, (B) second order and (C) Lagergren kinetics models of Cd(II) adsorption on to the composite at 450 mg L^{-1} initial Cd(II) concentration.

Characterization of the composite

The optimum performance sample A_{700} has been characterized using FTIR, XRD and SEM techniques.

Fourier transform spectroscopy

In the IR of CG-g-PAM, merged amide I and amide II peak is seen as broad intense peak at 1663 cm^{-1} along with the O-H, C-H stretchings at 3412 and 2929 cm^{-1} respectively as in CG gum (spectra not shown). However in A_{700} the incorporation of inorganic component can be identified from the Si-O-Si modes observed below 1250 cm^{-1} (Fig. 5a). Peak is visible at 459 cm^{-1} (due to oxygen ring breathing mode, involving four membered rings (cyclic tetrasiloxanes) or a symmetric oxygen stretching vibrations of Q^3 surface silanol sites [25], at 792 cm^{-1} (symmetric Si-

O-Si stretching vibrations). LO and TO Si-O-Si asymmetric stretching modes are seen as merged broad peak at 1091 cm^{-1} . A broad SiO-H absorption band is visible at 3429 cm^{-1} .

IR of the cadmium loaded hybrid showed Si-O-Si stretching modes at 1201 cm^{-1} , oxygen ring breathing mode at 464 cm^{-1} , symmetric Si-O-Si stretching vibrations at 798 cm^{-1} , Si-OH stretching, Si-O-Si asymmetric stretching modes as merged broad peak at 1091 cm^{-1} and a broad SiO-H absorption band at 3411 cm^{-1} .

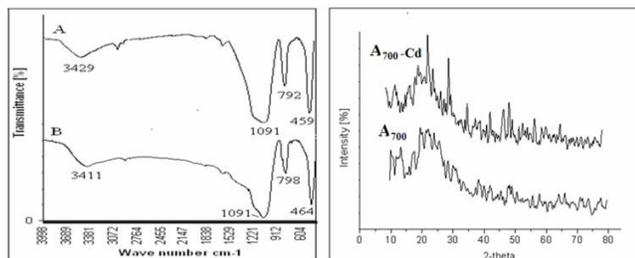


Fig. 5 (a). IR spectra of (A) A₇₀₀ (B) A₇₀₀-Cd; (b) XRD of A₇₀₀ and A₇₀₀-Cd.

Certain amount of peak shifts are visible in the cadmium loaded hybrid, being major for SiO-H modes (from 3439 to 3411 cm^{-1}), indicating their involvement in the cadmium binding.

X-ray diffraction

The X-ray diffraction pattern (**Fig. 5b**) showed that the hybrids retained their amorphous characters even on thermal treatment until 700 °C (A₇₀₀) and showed a broad hollow, typical of amorphous material, however the Cd (II) loaded adsorbent show crystalline peaks in the region of 2-theta 23.6 , 30.35 , 49.8 , that give concrete evidence for cadmium sorption on to the hybrids.

Scanning electron microscopy

The cadmium loading on to A₇₀₀ is confirmed by morphological changes observed in the SEM picture. In the loaded samples the cadmium deposits are seen as small balls on to the surface of the composite. Cd loading on to the adsorbent is further evidenced by comparing EDAX spectra of the Cd(II) loaded sample with the adsorbent (**Fig. 6**).

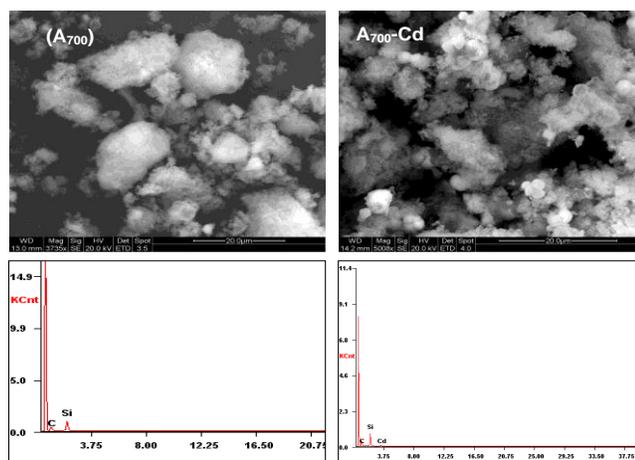


Fig. 6. SEM picture & EDX of A₇₀₀ and A₇₀₀-Cd.

Conclusion

The composite synthesized from *Cassia grandis* seed gum-graft-poly(acrylamide) templated polymerization of TEOS on calcination at 700 °C furnished an adsorbent which showed unprecedented Cd(II) adsorption (Q_{max} of 5000 mg g^{-1}) at pH 8. The composite can be distinguished by its high adsorption capability, reusability, stability and versatile applicability. The reusability of the bioinspired adsorbent was tested for three consecutive cycles where almost negligible loss in its adsorption capacity was witnessed. The present adsorbent showed 2.5 times higher Q_{max} and 3.2 times shorter equilibrium time than our previously reported adsorbent that was similarly derived from guar gum. This indicates that other than the calcination temperature and TEOS:H₂O ratio, the polysaccharide's structure plays an important role in deciding the microstructure and performance of the synthesized adsorbents. Thus the adsorbent is economical and industrially viable and lucrative material for the removal of cadmium ions from industrial waste and mining discharges.

Acknowledgements

Authors acknowledge Department of Science and Technology, New Delhi, India for the financial support to carry out the present work.

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